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DISSEMINATION APPARATUS

This invention relates to apparatus for the disseminating of volatile liquids into an atmosphere.

- 5 One very common method apparatus for disseminating a volatile liquid, such as a fragrance or an insecticide, into an atmosphere consists of a porous transfer member, such as a porous wick, that is in contact with a reservoir of volatile liquid. Liquid rises up this wick and evaporates into the atmosphere. This system has drawbacks, such as the low surface area for evaporation and the tendency for the wick to fractionate complex mixtures, such as fragrances, so that some
10 components are disseminated earlier than others and the full effect of the fragrance is lost.

It has been proposed to overcome this disadvantage by using external capillaries, that is, capillary channels cut or moulded into a suitable substrate. One example is described in United States Patent 4,913,350, in which an external capillary channel-containing member is inserted
15 into a liquid. In another embodiment, described in United Kingdom Patent Application GB 0306449, there is fitted to a known transfer member a capillary sheet, that is, a sheet extending essentially perpendicularly from the transfer member and comprising channels of capillary dimensions, to which volatile liquid can pass and travel along for evaporation. This sheet generally contacts the transfer member by means of a hole in the sheet through which the
20 transfer member protrudes and within which it fits snugly, at least some of these channels contacting the transfer member such that liquid can transfer from the member to the sheet ("liquid transfer contact").

Although this technology offers significant advantages over the porous wicks of the art, these
25 advantages have never been completely realized. It has now been found that it is possible to obtain the full benefits of the technology by adherence to certain fundamental parameters. The invention therefore provides an apparatus adapted to disseminate volatile liquid into an atmosphere from a reservoir, the transfer to atmosphere being at least partially achieved by means of a transfer member having external capillary channels, characterised in that

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- (a) at least 30% by weight of the materials comprising the volatile liquid have a molecular weight of 175 maximum and the volatile liquid has a surface tension of less than 40 dynes/cm; and

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(b) The transfer member is of plastics material having a surface energy of less than 45 dyne/cm.

By "at least 30% by weight" is meant all the components of the liquid, including any solvent 5 present.

When the active is a fragrance it can be composed with one or more compounds, for example, natural products such as extracts, essential oils, absolutes, resinoids, resins, concretes etc., but also synthetic materials such as hydrocarbons, alcohols, aldehydes, ketones, ethers, acids, 10 esters, acetals, ketals, nitrites, etc., including saturated and unsaturated compounds, aliphatic, carbocyclic, and heterocyclic compounds. The molecular weights range from around 90 to 320. Such fragrance materials are mentioned, for example, in S. Arctander, Perfume and Flavor Chemicals (Montclair, NJ., 1969), in S. Arctander, perfume and Flavor Materials of Natural Origin (Elizabeth, N.J., 1960) and in "Flavor and Fragrance Materials--1991", 15 Allured Publishing Co. Wheaton, Ill. USA.

Some non-limiting examples of useful volatile materials whose molecular weight is less than 175 are:

Material	Molecular Weight
ethyl acetate	88
iso-amyl alcohol	88
2-methylpyrazine	94
cis 3-hexenol	100
C6-aldehyde	100
C6 alcohol	102
ethyl propionate	102
benzaldehyde	106
benzyl alcohol	108
C7-aldehyde	114
methyl amyl ketone	114
iso amyl formate	116

ethyl butyrate	116
Indole	117
acetophenone	120
phenyl ethyl alcohol	122
styralyl alcohol	122
Veltol™	126
methyl hexyl ketone	128
3-methyl 3-methoxy butanol	128
ethyl amyl ketone	128
octenol JD	128
prenyl acetate	128
C8-aldehyde	128
amyl acetate	130
cinnamic aldehyde	132
phenyl propyl aldehyde	134
cinnamic alcohol	134
terpinolene	136
phenyl acetic acid	136
phenyl propyl alcohol	136
alpha pinene	136
benzyl formate	136
anisic aldehyde	136
d-limonene	136
Triplal™	138
Cyclal C™	138
Melonal™	140
C-9 aldehyde	142
iso nonyl aldehyde	142
cyclo hexyl acetate	142
ethyl caproate	144
hexyl acetate	144
coumarin	146

methyl cinnamic aldehyde	146
cuminic aldehyde	148
benzyl acetone	148
geranyl nitrile	149
cuminal alcohol	150
benzyl acetate	150
Heliotropine™	150
thymol	150
neral	152
synthetic vanillin	152
synthetic citral	152
rose oxide	154
geraniol	154
allyl caproate	156
Rosalva™	156
tetrahydro myrcenol	158
yara yara	158
diethyl malonate	160
methyl cinnamate	162
Jasmorange™	162
benzyl propionate	164
eugenol	164
ethyl vanillin	166
dihydrojasmone	166
geranic acid	168
methyl laitone	168
methyl nonyl ketone	170
methyl tuberate	170
hexyl butyrate	172
octyl-3-acetate	172
hydroxycitronellol	174
Fructone™	174

Some non-limiting examples of useful materials that can be used that have a molecular weight higher than 175 are:

Material	Molecular Weight
benzal glyceryl acetal	180
anisyl acetate	180
terpinyl formate	182
geranyl formate	182
methyl diphenyl ether	184
delta undecalactone	184
allyl amyl glycolate	186
amyl caproate	186
Fraistone™	188
Pelargene™	188
Florhydral™	190
ethyl hexyl ketone	190
ethyl phenyl glycidate	192
Verdyl acetate™	192
dihydro beta ionone	194
iso-butyl salicylate	194
allyl cyclo hexyl propionate	196
myrcenyl acetate	196
citronellyl oxyacetaldehyde	198
citral dimethyl acetal	198
beta naphthyl iso butyl ether	200
tetrahydro linalyl acetate	200
amyl cinnamic aldehyde	202
Fruitaflor™	202
Lilial™	204
damascenone	204
methyl ionone	206

Cashmeran™	206
Ebanol™	206
phenoxy ethyl iso butyrate	208
iso amyl salicylate	208
Sandalore™	210
propyl dianthilis	210
benzyl benzoate	212
citronellyl propionate	212
myristic alcohol	214
Gelsone™	214
hexyl cinnamic aldehyde	216
butyl butyryllactate	216
amyl cinnamate	218
hydroxycitronellal dimethyl acetal	218
beta methyl ional	220
Vetiverol™	220
hexyl salicylate	222
geranyl crotonate	222
methyl jasmonate	224
linalyl butyrate	224
Hedione™	226
Timberol™	226
Floramat™	228
benzyl salicylate	228
Fixal™	230
Cetone V™	232
cis carveol	232
Iso E Super™	234
muscalone	234
geranyl tiglate	236
Cetalox™	236
linalyl valerate	238

benzyl cinnamate	238
Thibetolide™	240
phenyl ethyl phenylacetate	240
phenyl ethyl salicylate	242
Boisambrene™	242
jasmonyl	244
Phantolid™	244
methyl cedryl ketone	246
Aldrone™	248
amyl cinnamic aldehyde dma	248
Dione™	250
cedryl formate	250
ambrettolide	252
phenyl ethyl cinnamate	252
benzyl iso eugenol	254
hexadecanolide	254
Novalide™	256
citronellyl ethoxalate	256
Fixolide™	258
Galaxolide™	258
rose acetate	262
ambrate	262
iso caryl acetate	264
cinnamyl cinnamate	264
ethyl undecylenate	266
Ethylene Brassylate™	272
triethyl citrate	276
dihexyl fumarate	284
Okoumal™	288
musk ketone	294
alpha Santalol™	300
geranyl iso valerate	312

The solvent of the volatile liquid can be selected from many classes of volatile compounds that known to the art, for example, ethers; straight or branched chain alcohols and diols; volatile silicones; dipropylene glycol, triethyl citrate, ethanol, isopropanol, diethyleneglycol monoethyl ether, dipropylene glycol, diethyl phthalate, triethyl citrate, isopropyl myristate, etc.,

- 5 hydrocarbon solvents such as IsoparTM or other known solvents that have previously been used to dispense volatile actives from substrates. These solvents in general have a molecular weight between 20 and 400. They are selected specifically for each volatile liquid to achieve the performance and safety, (e.g. VOC and flash point) specified.
- 10 When the active is an insect repellant it can be composed of one or more compounds such as pyrethrum and pyrethroid type materials commonly now used in mosquito coils are likely to be the most useful for this purpose. Other insect control actives can be used, such as the repellants DEET, essential oils, such as citronella, lemon grass oil, lavender oil, cinnamon oil, neem oil, clove oil, sandalwood oil and geraniol.
- 15 When the active is an antimicrobial it can be composed of one or more of compounds such as essential oils such as rosemary, thyme, lavender, eugenic, geranium, tea tree, clove, lemon grass, peppermint, or their active components such as anethole, thymol, eucalyptol, farnesol, menthol, limonene, methyl salicylate, salicylic acid, terpineol, nerolidol, geraniol, and mixtures thereof. benzyl alcohol, ethylene glycol phenyl ether, propylene glycol phenyl ether, propylene carbonate, phenoxyethanol, dimethyl malonate, dimethyl succinate, diethyl succinate, dibutyl succinate, dimethyl glutarate, diethyl glutarate, dibutyl glutarate, dimethyl adipate, diethyl adipate, dibutyl adipate, or mixtures thereof one or more aldehydes selected from cinnamic aldehyde, benzaldehyde, phenyl acetaldehyde, heptylaldehyde, octylaldehyde, decylaldehyde, undecylaldehyde, undecylenic aldehyde, dodecylaldehyde, tridecylaldehyde, methylnonyl aldehyde, didecylaldehyde, anisaldehyde, citronellal, citronellyloxyaldehyde, cyclamen aldehyde, alpha-hexyl cinnamic aldehyde, hydroxycitronellal, alpha-methyl cinnamic aldehyde, methylnonyl acetaldehyde, propylphenyl aldehyde, citral, perilla aldehyde, tolylaldehyde, tolylacetaldehyde, cuminaldehyde, LilialTM, salicyl aldehyde, alpha-amylcinnamic aldehyde and HeliotropineTM.

Other volatile actives can be used alone or in combination with the above actives, for example decongestants such as menthol, camphor, eucalyptus etc., malodor counteractants such as are

trimethyl hexanal, other alkyl aldehydes, benzaldehyde, and vanillin, esters of alpha-, beta-unsaturated monocarboxylic acids, alkyl cyclohexyl alkyl ketones, derivatives of acetic and propionic acids, 4-cyclohexyl-4-methyl-2-pentanone, aromatic unsaturated carboxylic esters, etc.

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Care must be taken when designing the volatile liquid in that they pose no danger to the public. This is done by ensuring that the said volatile liquid has a flashpoint greater than about 60°C as determined by Test Method ASTM D93.

10 The transfer medium must have external capillary channels, that is, channels of capillary dimensions provided on an external surface of the medium such that a liquid will exhibit capillary flow within them. These may be provided by any suitable means, such as moulding and engraving. The transfer medium may be any suitable form of such medium, but is preferably one of two kinds:

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1. The type in which a member bearing external capillary channels contacts directly a liquid in a reservoir, and the liquid rises in the capillary channels and evaporates into the atmosphere. An example of such a type is described in US 4,193,350

20 2. A type in which the liquid in the reservoir is taken therefrom by a porous wick in contact with it, there being mounted on the wick a capillary sheet whose external capillary channels are in liquid transfer contact with the wick, the liquid passing from the wick to the capillary channels and evaporating into the atmosphere. An example of such an apparatus is described in UK patent application GB 0306449

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For the working of this invention, it is essential that the volatile liquid have a surface tension of 40 dynes/cm maximum and that the plastics material have a surface energy of 45 dynes/cm maximum. It has been found that this combination of parameters allows for an especially good dissemination of a liquid into an atmosphere. The invention therefore also provides a method of 30 disseminating a volatile liquid into an atmosphere by evaporation from a transfer member having surface capillary channels, the volatile liquid being such that at least 30% by weight of the materials comprising it have a molecular weight of 175 maximum, and that it has a surface

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tension of less than 40 dynes/cm, and the transfer member being of plastics material having a surface energy of less than 45 dyne/cm.

The provision of a volatile liquid having the abovementioned characteristics is well within the
5 skill of the art.

Preferably the liquid has a surface tension of less than 40 dyne/cm, and is more preferably within the range 20-35 dynes/cm. All surface tensions referred to herein are measured on a Fisher Surface Tensiomat model number 21 at 25°C.

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It is further preferred that the volatile liquid have a viscosity of less than 10 centistokes per second at 25°C as measured on a Cannon-Fenske Viscometer according to Test Method ASTM D 445.

15 The plastics materials for use in this invention preferably have a surface energy of from 15-45 dyne/cm. The surface energy of a plastics material is dependent upon its molecular structure and is a measure of the ability of a surface to be wetted. The more inert is a plastics material chemically, the lower is its surface energy. Thus, materials such as polyethylene, polypropylene and PTFE have low surface energies, whereas the plastics with more polar groups have higher
20 surface energies. Preferably the surface energy lies in the range of from 30-45 dynes/cm and more preferably from 30-35 dyne/cm. Some suitable materials for the purposes of this invention are shown in the following table:

Material Name	Example Material Trade Name(s)	Supplier	Surface Energy Dynes/cm
Polytetrafluoroethylene PTFE	TEFLON FEP106N	DU PONT	18
Polyethylene PE (HDPE)	BOREALIS MG 9641-R	NORTHERN PLASTICS	30
Polyethylene PE (LDPE)	IPETHENE 320	CARMEL OLEFINS	30
Polyethylene PE (LLDPE)	LL6201	EXXON MOBIL	30
Polystyrene PS	PS 146L	NOVA CHEMICALS	36

Polyvinylchloride PVC			41
Polyethylene terephthalate PET	RADITER	RADICI (PLASTRIBUTIO N)	42
Polycarbonate PC	LUPILON S- 3000R	MITSUBISHI POLYMERS	40
Polyvinylpropylene PP	EXP 058	EXXON MOBIL	32

(TEFLON, BOREALIS, IPETHENE, RADITER and LUPILON are trade marks)

Suitable transfer members may be easily fabricated by known means, for example, by the
 5 methods described in the abovementioned US 4,913,350 and GB application 0306449.

The invention is further described by the following non-limiting examples.

Example 1.

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Capillary sheets of polypropylene BP 400Ca 70, measuring 2.5 cm x 7.5 cm and having a surface energy of 32 dyne/cm, were immersed to a depth of 1.25 cm. into 10g of a number of vanilla fragrances containing different amounts of volatile materials with a MW less than 175. The quantity of fragrance diffused into the air was determined by weighing the container with
 15 fragrance and capillary. The following results were obtained after 4 days.

Fragrance	% MW < 175	Wt loss g/day
A1	14.5	0.35
A2	34.5	0.87
A3	53.6	0.64
A4	61.6	0.69
A5	69.05	1.10
A6	75.6	0.84
A7	81.6	0.86
A8	93.5	0.97
A9	93.5	1.07

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This shows that, for effective transmission of fragrance into the atmosphere, the composition must have at least 30% of the fragrance materials with a molecular weight of less than 175.

Example 2

- 5 Two frusto-conical polyester wicks were placed in 11.5 g of A1 and A2 fragrances in BarexTM containers and allowed to equilibrate overnight. 1.5 mm thick polypropylene external capillary sheets with a central hole that allowed them to be fitted to the wicks were placed thereon, and the quantity of fragrance diffused per day was measured. The results after 6 days are shown below:

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Fragrance	% MW < 175	Weight Loss g/day
A1	14.5	0.4
A2	35.5	1.0

For a hybrid system i.e. one in which the transport of the fragrance is via a porous wick and the diffusion is via an external capillary, good diffusion is obtained when the fragrance has a quantity of components with a MW < 175 is around 30% or higher

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Example 3.

- Capillary sheets of polypropylene BP 400Ca 70, measuring 2.5cm x 7.5 cm external capillary and having a surface energy of 32 dyne/cm, were immersed to a depth of 1.25cm into 10g of a
20 series of fragrances having more than 30% components with MW < 175, but with different surface tensions. The surface tension was measured at 25 C using a Fisher Surface Tensiomat model number 21.

- The quantity of fragrance diffused into the air was determined by weighing the container with
25 fragrance and capillary. The following results were obtained after 2 days:

Fragrance	Wt Loss g/day	Surface tension Dynes/cm
B1	1.1	35.6
B2	0.7	38.2
B3	0.5	41.2
B4	0.5	42.2

This shows the advantage of having a surface tension below 40, and preferably below 38, dynes/cm.

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Example 4.

A capillary sheet of polypropylene BP 400Ca 70, measuring 2.5cm x 7.5 cm and having a surface energy of 32 dyne/cm, was immersed to a depth of 1.25cm into 10g of a series of 10 fragrances having more than 30% components with MW < 175, but with different viscosities, The viscosity was measured using a Cannon-Fenske Viscometer by ASTM D 445 .

The quantity of fragrance diffused into the air was determined by weighing the container with fragrance and capillary. The following results were obtained after 2 days:

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Fragrance	Wt Loss g/day	Viscosity Cs/s
C1	0.4	13.7
C2	0.4	11.9
C3	0.4	10.6
C4	0.9	8.2
C5	1.1	6.0

For good diffusion, the viscosity of the fragrance should be below 10 Cs/s.

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Example 5.

Capillary sheets with different surface energies were set up as per example 1 with fragrance D (% Components MW<175 > 30, surface tension 37 dynes/cm and viscosity 5.7 cS/s) and 5 fragrance E (% Components MW<175 > 30, Viscosity 2.9 cS/s and surface tension 34.5 dynes/sec), respectively. The fragrances had an oil-soluble dye added and the height to which it rose (as a percentage of the height of the capillary) after 6 minutes was measured and recorded, and is shown in the following tables.

10 Table 5 Effect of surface energy on diffusion of fragrance D

Plastic	Surface energy dyne/cm	Rise 6 min
PP BP 400	32	100(3)
PETG	41	81
PB ABS	46	59

The 100% rise in PP BP 400 was achieved after only 3 minutes.

Table 6 Effect of surface energy on diffusion of fragrance E.

Plastic	Surface energy dynes/cm	Rise 6 min
PP BP 400	32	100(1.2)
PETG	41	100(2)
PB ABS	46	41

100% rise was found after 1.2 min and 2 min, respectively for PP BP 400 and PETG.

This shows that the surface energy of the plastics material of the external capillary should be below 45 dynes/cm, preferably below 40 dynes/cm.

Claims:

1. An apparatus adapted to disseminate volatile liquid into an atmosphere from a reservoir, the transfer to atmosphere being at least partially achieved by means of a transfer member
5 having external capillary channels, characterised in that
 - (a) at least 30% by weight of the materials comprising the volatile liquid have a molecular weight of 175 maximum and the volatile liquid has a surface tension of less than 40 dynes/cm; and
 - 10 (b) the transfer member is of plastics material having a surface energy of less than 45 dyne/cm.
2. An apparatus according to claim 1, in which the surface tension of the liquid is from 20-35 dynes/cm.
15
3. An apparatus according to claim 1, in which the surface energy of the plastics material is from 15-45 dynes/cm.
4. An apparatus according to claim 3, in which the surface energy lies in the range of from
20 30-45 dynes/cm.
5. An apparatus according to claim 4, in which the surface energy lies in the range of from
25 30-35 dynes/cm.
6. An apparatus according to claim 1, in which the volatile liquid has a viscosity of less than 10 centistokes per second at 25°C.
30
7. An apparatus according to claim 1 in which the transfer member bears external capillary channels, which directly contact a liquid in a reservoir, and the liquid rises in the capillary channels and evaporates into the atmosphere.
8. An apparatus according to claim 1, in which the liquid in the reservoir is taken therefrom by a porous wick in contact with it, there being mounted on the wick a capillary sheet

whose external capillary channels are in liquid transfer contact with the wick, the liquid passing from the wick to the capillary channels and evaporating into the atmosphere.

9. A method of disseminating a volatile liquid into an atmosphere by evaporation from a transfer member having surface capillary channels, the volatile liquid being such that at least 30% by weight of the materials comprising it have a molecular weight of 175 maximum, and that it has a surface tension of less than 40 dynes/cm, and the transfer member being of plastics material having a surface energy of less than 45 dyne/cm.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/CH2004/000647

A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 A61L9/00 A61L9/12 A61L9/04 A01M1/20 A01M13/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 A61L A01M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 02/34302 A (JONES STUART MICHAEL RUAN ; RECKITT BENCKISER UK LTD (GB)) 2 May 2002 (2002-05-02) page 5, line 22 - page 6, line 10; claim 5; figures	1-6,8
Y	GB 2 357 973 A (RECKITT BENCKISER ; RECKITT & COLMAN PROD LTD (GB)) 11 July 2001 (2001-07-11) page 1, lines 3-8 page 3, line 1 - page 4, line 9 page 7, line 24 - page 8, line 12; figures	9
X	WO 02/30220 A (WOLPERT CHRISTOPHER J ; DIAL CORP (US); TRIPPLETT CARL (US); HE MENGTAO) 18 April 2002 (2002-04-18) figures; example 1	1-7
Y		9
		-/-

 Further documents are listed in the continuation of box C. Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the International search 22 December 2004	Date of mailing of the International search report 13/01/2005
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patenttaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax (+31-70) 340-3016	Authorized officer Persichini, C

INTERNATIONAL SEARCH REPORT

International Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 180 450 A (MEDICAL EXPRESS) 1 April 1987 (1987-04-01) page 3, lines 10-30 page 4, lines 10-15 -----	1-7
Y	US 4 913 350 A (PURZYCKI KENNETH L) 3 April 1990 (1990-04-03) cited in the application figures; example 4 -----	9

INTERNATIONAL SEARCH REPORT

International Application No PCT/CH2004/000647

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